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[Document] Abstract 1



[Document Name] Specification

[Title of the Invention] Process for Forming Semiconductor Film,  
and Photoelectrode

[Claims]

5                   [Claim 1] A process for forming a semiconductor film  
comprising the step of applying a semiconductor particle  
dispersion liquid to a surface of a substrate by spray coating in  
such a manner that the atomized droplets of the dispersion liquid  
discharged from the spray coater have a mean diameter of 20  $\mu\text{m}$  or  
10 less.

                  [Claim 2] The process according to claim 1, wherein the  
semiconductor particle dispersion liquid is a dispersion of  
titanium particles in methanol and/or ethanol.

                  [Claim 3] The process according to claim 1 or 2,  
15 wherein the substrate is a high polymer film.

                  [Claim 4] A semiconductor film obtained by a process  
according to any one of claims 1, 2 and 3, used for photoactivity,  
bacteria prevention, hydrophilization, stain prevention, anti-  
fogging, gas decomposition, deodorization, water treatment, or  
20 energy conversion.

                  [Claim 5] A photoelectrode comprising a laminate that  
comprises a transparent high polymer film layer, a transparent  
electrode layer, and a semiconductor film prepared by a process  
according to any one of claims 1, 2 and 3.

25 [Detailed Description of the Invention]

[0001]

                  [Field of the Invention] The present invention relates  
to a process for forming a semiconductor film that is excellent  
in photoactivity, antibacterial properties, hydrophilicity, stain  
30 resistance, anti-fogging properties, gas decomposing properties,  
deodorizing properties, water-treating capabilities, energy  
conversion properties and other properties, a photoelectrode  
prepared using the semiconductor film.

[0002]

35 [Prior Art and Problems Thereof] Semiconductor

particles such as titanium oxide have photoactivity, antibacterial properties, hydrophilicity, stain resistance, anti-fogging properties, gas decomposing properties, deodorizing properties, water-treating capabilities, energy conversion properties and other properties, and thus are used in a variety of fields. In particular, solar cells, photoelectric conversion materials, etc. are attracting attention as means for producing motive power, heat and other energies without adverse effects on the global environment.

10 [0003]

With regard to processes for forming a semiconductor film using particles of a semiconductor such as titanium oxide, Japanese Unexamined Patent Publication No. 1998-212120 discloses a process comprising applying a dispersion of titanium oxide particles in a solvent, such as polyethylene glycol, onto a glass, metal, ceramic or like substrate by spray coating, dip coating or like method, and then sintering the coating at 200 to 800°C.

[0004]

Further, Japanese Unexamined Patent Publication No. 2002-145615 discloses a process for forming a porous titanium oxide film on a substrate, comprising intermittently spraying a starting solution containing a titanium oxide precursor, onto a substrate, such as glass, maintained at a high temperature so as to thermally decompose the titanium oxide precursor to titanium oxide.

[0005]

In these processes, a titanium oxide solution is sintered at a temperature of 200°C or more to form a porous titanium oxide film, and therefore they have a drawback in that they are not applicable to thermoplastic resins or like substrates (such as sheets, films, moldings, etc.) that deform or degrade at temperatures less than 200°C.

[0006]

Japanese Unexamined Patent Publication No. 1999-204152 discloses a process comprising applying a dispersion of metal

oxide particles in a high polymer material to a plastic substrate by dip coating or spray coating, and drying the dispersion at a temperature of 200°C or lower.

[0007]

5           This process employs a relatively low sintering temperature, and was developed for application to thermoplastic resin substrates. However, the metal oxide particles used in the process is a colloidal dispersion sol of metal alkoxide, such as titanium alkoxide, and when such a sol is sprayed onto a plastic  
10 sheet, the resulting titanium oxide film has good adhesion but has a small roughness factor (porosity) and inferior photoelectric conversion efficiency.

[0008]

          An object of the present invention is to provide a  
15 process for forming a semiconductor film that is free from the problems of the prior art, i.e., has excellent adhesion to substrates, in particular high polymer films, and excellent photoelectric conversion efficiency, and a photoelectrode prepared using the semiconductor film.

20           [0009]

          [Patent Document 1]

          Japanese Unexamined Patent Publication No. 2002-145615

          [Patent Document 2]

          Japanese Unexamined Patent publication No. 1999-204152

25           [0010]

          [Means for Solving the Problems] The present inventors found that all the problems described above can be solved by forming a semiconductor film while controlling the atomized droplets of the dispersion liquid discharged from the spray  
30 coater to have a mean diameter of 20  $\mu\text{m}$  or less, accomplishing the present invention.

[0011]

          The present invention provides:

          1. A process for forming a semiconductor film  
35 comprising the step of applying a semiconductor particle

dispersion liquid to a surface of a substrate by spray coating in such a manner that the atomized droplets of the dispersion liquid discharged from the spray coater have a mean diameter of 20  $\mu\text{m}$  or less.

5                   2. The process according to item 1, wherein the semiconductor particle dispersion liquid is a dispersion of titanium particles in methanol and/or ethanol.

                  3. The process according to item 1 or 2, wherein the substrate is a high polymer film.

10                   4. A semiconductor film prepared by a process according to any one of items 1, 2 and 3, used for photoactivity, bacteria prevention, hydrophilization, stain prevention, anti-fogging, gas decomposition, deodorization, water treatment, or energy conversion.

15                   5. A photoelectrode comprising a laminate that comprises a transparent high polymer film layer, a transparent electrode layer, and a semiconductor film prepared by a process according to any one of items 1, 2 and 3.

[0012]

20 [Mode for Carrying out the Invention] The present invention is described below in detail.

[0013]

                  The semiconductor particle dispersion liquid for use in the process of the present invention is obtained by dispersing  
25 semiconductor particles in a solvent.

[0014]

                  The semiconductor particles are not limited and may be any known semiconductor particles. Usable semiconductors include titanium oxide, zinc oxide, manganese oxide, cadmium oxide,  
30 indium oxide, lead oxide, molybdenum oxide, tungsten oxide, antimony oxide, bismuth oxide, copper oxide, mercury oxide, silver oxide, manganese oxide, iron oxide, vanadium oxide, tin oxide, zirconium oxide, strontium oxide, gallium oxide, silicon oxide, chromium oxide and other metal oxides;  $\text{SrTiO}_3$ ,  $\text{CaTiO}_3$  and  
35 other perovskites; cadmium sulfide, zinc sulfide, indium sulfide,

lead sulfide, molybdenum sulfide, tungsten sulfide, antimony sulfide, bismuth sulfide, cadmium zinc sulfide, copper sulfide and other metal sulfides; CdSe, In<sub>2</sub>Se<sub>3</sub>, WSe<sub>2</sub>, HgS, PbSe, CdTe and other metal chalcogenides; and GaAs, Si, Se, Cd<sub>2</sub>P<sub>3</sub>, Zn<sub>2</sub>P<sub>3</sub>, InP, AgBr, PbI<sub>2</sub>, HgI<sub>2</sub>, BiI<sub>3</sub> and other semiconductors. Also usable are composites comprising at least one member selected from the above semiconductors.

[0015]

Preferable semiconductor particles are anatase-type titanium oxide particles, which are inexpensive and has excellent performance. Commercial products of titanium oxide include "AMT-600" (tradename of TAYCA, anatase-type, mean particle size: 30 nm), "AMT-100" (tradename of TAYCA, anatase-type, mean primary particle size: 6 nm), "ST-01" (tradename of Ishihara Techno, anatase-type, mean primary particle size: 7 nm), "ST-21" (tradename of Ishihara Techno, anatase-type, mean primary particle size: 20 nm), "P-25" (tradename of Nippon Aerosil, rutile-anatase type, mean primary particle size: about 30 nm), etc.

[0016]

The mean primary particle size of the semiconductor particles is, for example, 1 nm to 1000 nm, and preferably 15 nm to 100 nm. When used for dye-sensitized solar cells (Graetzel cells), semiconductor particles with a mean primary particle size of less than 10 nm are not preferable, since the use of such particles leads to a semiconductor layer with a small mean pore size, making it difficult to transfer redox substances in the electrolyte solution and to adsorb the sensitizing dye. As a result, the current value after photoelectric conversion is low. Similarly, semiconductor particles with a mean particle size greater than 1000 nm are not preferable since use of such particles leads to a semiconductor layer that has too small a surface area to support a sufficient amount of sensitizing dye, resulting in a low current value after photoelectric conversion. Since semiconductor particles usually aggregate into secondary

particles, they are preferably dispersed using a dispersing device to obtain particles having the mean primary particle size or a mean particle size approximate to the mean primary particle size. The mean particle size of the semiconductor particles after  
5 dispersion using the dispersing device is preferably about 100 nm or less.

[0017]

Preferable solvents for dispersing the semiconductor particles include methanol and ethanol. In addition to these  
10 solvents, known organic solvents can be used, including, for example, water; xylene, toluene, and other aromatic solvents; methanol, ethanol, n-propanol, isopropanol, n-butanol, polyalkylene glycols and other alcoholic solvents; diethylene glycol, diethylene glycol monoethyl ether, diethylene glycol  
15 monobutyl ether, triethylene glycol monomethyl ether, polyoxyalkylene glycol derivatives (e.g., polyoxyethylene(10)octylphenyl ether) and other ethereal solvents; acetone, methyl ethyl ketone and other ketonic solvents; methyl acetate, ethyl acetate, propyl acetate, butyl  
20 acetate, isobutyl acetate and other ester solvents; etc.

[0018]

The dispersion liquid may contain, in addition to the above materials, known complexing agents (e.g., acetyl acetone), dispersing resins, etc.

25 [0019]

The substrate for use in the process of the present invention is not limited and may be selected from various known substrates. Specifically, usable substrates include high polymer films, glass, metals, concretes, coating films, etc., among which  
30 high polymer films are preferable in the present invention. Preferable materials for high polymer films include polyethylene terephthalate, silicon resins, fluororesins, acrylic resins, etc. From the viewpoint of practical use, polyethylene terephthalate is particularly preferable.

35 [0020]



The semiconductor particle dispersion liquid for use in the present invention preferably has a solids content of 1 wt.% to 40 wt.%, and preferably 5 to 30 wt.%, at the time of spray coating. When the dispersion liquid has a solids content less than 1 wt.%, it is difficult to obtain the necessary film thickness, with the result that the obtained semiconductor film is liable to have insufficient photoelectric conversion efficiency. Moreover, with such a solids content, the dispersion liquid as deposited is unlikely to have an adequate solids content (usually 90 wt.% or more) controlled by spray coating, which is a feature of the present invention. This makes it difficult to obtain a thin semiconductor film that is porous and has good adhesion.

When the dispersion liquid has a solids content of more than 40 wt.%, the mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is large, and a semiconductor film with excellent photoelectric conversion efficiency cannot be obtained. Moreover, when the dispersion liquid has a high solids content, the movement of the semiconductor particles in the atomized droplets of the dispersion liquid is restricted, resulting that the semiconductor particle binding energy, which is a feature of the present invention, produced by the sharp decrease of the kinetic energy of the semiconductor particles from the start of the spraying of the dispersion liquid until the deposition on the substrate, is reduced. Thus, a thin semiconductor film with good adhesion and high strength cannot be obtained.

[0021]

The dispersion liquid to be applied by spray coating preferably has a viscosity of 0.001 Pa·sec to 1 Pa·sec, and more preferably 0.001 Pa·sec to 0.1 Pa·sec. When the viscosity is less than 0.001 Pa·sec, the dispersion liquid is imparted with only a low energy by spraying, and therefore the semiconductor particles have a low initial energy, and a thin semiconductor film with good adhesion cannot be obtained. When the dispersion liquid has

a viscosity of more than 1 Pa·sec, atomization of the dispersion liquid into droplets, which is a feature of the present invention, is difficult, and a thin semiconductor film with good adhesion cannot be obtained.

5 [0022]

Examples of spray coaters usable in the process of the present invention include electrostatic spray coaters, non-electrostatic spray coaters, rotary spray coaters, magnetic spray coaters, ultrasonic atomizers and other known spray coaters.

10 Electrostatic spray coaters and ultrasonic atomizers are particularly preferable. Preferably usable nozzles include two-fluid spray nozzles that can form atomized droplets with a narrow particle size distribution.

[0023]

15 Optimal spraying conditions for such spray coaters, such as nozzle type, atomization air pressure, pattern width, discharge amount, discharge pressure, coating speed, number of stages (number of coating applications), nozzle-substrate distance, etc., vary depending on the type of the coater used,  
20 and thus suitable conditions are selected according to the type of coater to be used, so that the atomized droplets of the dispersion liquid discharged from the spray coater has a mean diameter of 20  $\mu\text{m}$  or less, preferably 1 to 20  $\mu\text{m}$ , and more preferably 1 to 15  $\mu\text{m}$ . When the atomized droplets of the  
25 dispersion liquid have a mean diameter of more than 20  $\mu\text{m}$ , it is likely that the dispersed particles clog the nozzle tip or that the atomized droplets of the dispersion liquid deposited on the substrate surface unevenly agglomerate, leading to a small roughness factor. As a result, a semiconductor film with good  
30 adhesion to the substrate and high photoelectric conversion efficiency cannot be obtained. Further, when the atomized droplets of the dispersion liquid have a large mean diameter, the solvent volatilizes only slowly, and thus the dispersion liquid deposited on the substrate has a low solids content, failing to  
35 attain sharp decrease of the kinetic energy of the semiconductor

particles in the atomized droplets, which is a feature of the present invention. Thus, sufficient binding energy cannot be obtained.

[0024]

5           Examples of suitable coating conditions are as follows:  
an atomization air pressure of 0.5 to 5.0 kgf/cm<sup>2</sup> and preferably  
1.0 to 3.0 kgf/cm<sup>2</sup>; a discharge amount of 1 to 500 g/min and  
preferably 10 to 100 g/min; a nozzle-substrate distance of 5 to  
100 cm and preferably 10 to 50 cm; a coating speed of 1 to 200  
10 m/min and preferably 10 to 100 m/min; a coating pitch of 5 to 100  
mm and preferably 10 to 30 mm; a stage number of 1 to 100 and  
preferably 1 to 10.

[0025]

15           In this specification and the appended claims, the mean  
diameter of the atomized droplets of the dispersion liquid  
discharged from the spray coater is measured using a "2600  
Particle Sizer" (tradename of Malvern). For the measurement, it  
is aligned to the center portion of the spray from the side of  
the spray gun, and the distance from the nozzle tip to the  
20 substrate was the same as in actual coating operation.

[0026]

25           The above-mentioned spray coating results in a film  
that has a larger mean pore size than films formed by other  
coating processes such as roller coating, and thus is capable of  
forming a porous semiconductor particle film or a semiconductor  
film with a large specific surface area. (The mean pore size and  
specific surface area can be measured by, for example, according  
to JIS R 1625.)

30           Examples of glass plates include soda-lime glass, which  
has cost and strength advantages; and no-alkali glass, which is  
free from influences of alkali elution.

[0027]

          The above-mentioned high polymer film preferably has  
high flexural strength and high transparency.

35           [0028]

It is usually preferable that the high polymer film be 1  $\mu$ m to 10 mm thick, and especially 5  $\mu$ m to 5 mm thick.

[0029]

With respect to the size of the high polymer film, for example, it is 1 cm to 10 m, preferably 5 cm to 5 m, and more preferably 10 cm to 2 m in width, and 1 cm or more, preferably 5 cm or more, and more preferably 10 cm or more in length. The shape of the high polymer film may be rectangular or square. Further, for instance, a rolled high polymer film strip may be used as cut to a desired size after being coated with the semiconductor particle dispersion liquid and sintered.

[0030]

Preferable materials for high polymer films include polyethylene terephthalate, triacetyl cellulose, polyethylene naphthalate, syndiotactic polystyrene, polyphenylene sulfide, polycarbonates, polyallylates, polysulfones, polyester sulfones, polyimides, polyether imides, cyclic polyolefins, phenoxy bromide, etc.

[0031]

The semiconductor particle dispersion liquid is sprayed onto the substrate and sintered to form a porous semiconductor film.

[0032]

Any sintering method can be employed as long as it can impart energy to the semiconductor particles. Examples of usable methods include allowing to stand at room temperature; heating in an electric furnace, gas furnace or like device; irradiation with electromagnetic waves such as ultraviolet rays, visible rays, infrared rays, ultrasonic waves, plasma discharges, corona discharges, microwaves, etc. Preferable electromagnetic waves include ultraviolet rays, visible rays, infrared rays and microwaves. Ultraviolet rays, visible rays, infrared rays (e.g., far-infrared rays and near-infrared rays) and ultrasonic waves can be obtained from xenon lamps, halogen lamps, tungsten lamps, Nernst lamps, Global lamps, mercury lamps, fluorescent lamps and

other lamps; LEDs; lasers (ArF excimer lasers, KrF excimer lasers, XeCl excimer lasers, Nd:YAG lasers); synchrotron radiation; sunlight; etc. Microwaves can be obtained from magnetron devices or the like.

5 [0033]

In sintering by microwave irradiation, the semiconductor particles can be sintered by selectively imparting energy to the semiconductor particles utilizing dielectric loss. Therefore, microwave sintering is more advantageous than thermal  
10 sintering in an electric furnace or like device, in that microwave sintering is substantially free from heat losses by heat transfer to the substrate or thermal degradation of the substrate, and can be performed in a short period of time.

[0034]

15 In microwave sintering, the dielectric constant varies depending on the composition (e.g., type of dispersion medium; type, properties, particle size and shape of the semiconductor particles; solids content, etc.) of the semiconductor particle dispersion liquid. Thus, suitable conditions, such as microwave  
20 radiation frequency, microwave power, and irradiation time, can be selected according to the composition.

[0035]

Suitable conditions for microwave irradiation are selected according to the type of the semiconductor particle  
25 dispersion liquid, and usually as follows: a frequency of 300 MHz to 300 GHz, preferably 600 MHz to 200 GHz, and more preferably 1 GHz to 100 GHz; an output of 0.01 kW to 10 kW, preferably 0.1 kW to 5 kW, and more preferably 0.2 kW to 1.0 kW; and an irradiation  
time of 1 second to 60 minutes, preferably 2 seconds to 30  
30 minutes, and more preferably 30 seconds to 20 minutes.

[0036]

Usable microwave devices include, for example, an electromagnetic wave thermal sintering device manufactured by Fujidenpa Kogyo Co., Ltd. (tradename "FMS-10-28", frequency: 28  
35 GHz, output: 1 to 10kW).

[0037]

This microwave device emits microwaves with a frequency of 28 GHz and a wavelength of 10.7 cm, which are shorter in wavelength than microwaves generated by household microwave ovens (frequency: 2.45 GHz, wavelength: 12 cm). Accordingly, the device is advantageous in that it can uniformly heat the coating layer to form a homogeneous semiconductor film, and that, even when used at a high output, does not cause sparking (e.g., at the edge). Therefore, the device is especially suitable for sintering semiconductor particles on the surface of a high polymer film with a large area.

[0038]

When sintering the semiconductor particles, heating is preferably performed in combination with electromagnetic irradiation. It is also preferable that the semiconductor particle layer contain a semiconductor particle precursor (which encompasses nanoparticles with a particle diameter less than 10 nm). Further, to remove unnecessary organic or other matter during sintering, the sintering may be performed under reduced pressure, under a blown stream (air, oxygen, nitrogen, an inert gas or other gas), or in an ozone atmosphere, an oxidizing atmosphere, a reducing atmosphere or like atmosphere, etc.

[0039]

When using the microwaves to sinter semiconductor particles applied on a high polymer film such as a polyethylene terephthalate film with a relatively low melting point, the sintering temperature is preferably a temperature at which polyethylene terephthalate does not deform or degrade. An example of such a temperature is 200°C or less, in particular about 150°C to about 180°C.

[0040]

Further, before microwave sintering, the back of the high polymer film (the side opposite to the side to be provided with the semiconductor film, the side opposite to the side to be irradiated with microwaves) may be provided with a plate with a

high thermal conductivity, such as a plate of iron, stainless steel, copper or like metal, or a glass plate or like inorganic plate, to release heat from the high polymer film.

[0041]

5           When the semiconductor coating formed on the high polymer film surface has a large area, microwaves are likely to unevenly sinter the semiconductor particles. Uniform sintering can be achieved by, for example, the following methods:

[0042]

10           (1) Partial irradiation of the semiconductor coating with microwaves is repeated several times as required so that finally the whole surface of the coating is irradiated, to thereby dissipate the heat generated by irradiation.

[0043]

15           (2) The high polymer film surface is partially coated with the semiconductor particle dispersion liquid so as to form a striped pattern, in order to prevent unnecessary heat generation.

[0044]

20           (3) The electrodes arranged on the high polymer film are masked with a polyimide film or like highly heat-resistant film, and the non-masked portion is coated with the semiconductor particle dispersion liquid, and then the resulting coating is irradiated with microwaves for sintering.

[0045]

25           (4) A high polymer film strip coated with the semiconductor particle dispersion liquid is moved with the dispersion liquid-coated surface being positioned perpendicularly to the direction of the microwave irradiation.

[0046]

30           Before partially or wholly irradiating the semiconductor particle dispersion liquid layer formed on the high polymer film surface with microwaves for sintering, a plate made of glass, tetrafluoroethylene or like material that transmits microwaves may as required be provided above the semiconductor  
35           particle coating layer, to thereby prevent sparks or like

problems. Further, to achieve uniform heating, the high polymer film is preferably pressed against and closely contacted with the worktable to thereby transfer excess heat generated by the microwave sintering to the worktable.

5 [0047]

Heating conditions can be selected according to the type of substrate. Specifically, for example, when using a glass plate, baking can be performed at a temperature of 300°C or higher. When using a high polymer film (polyethylene terephthalate),  
10 baking can be performed at a temperature of about 200°C or lower, and more preferably about 150°C to about 180°C.

[0048]

In the process of the present invention, the thickness of the semiconductor film can be suitably selected according to  
15 the intended use, and is usually 1  $\mu\text{m}$  to 100  $\mu\text{m}$ , and preferably 2  $\mu\text{m}$  to 50  $\mu\text{m}$ .

[0049]

Many of semiconductor films formed according to the process of the present invention are activated by light  
20 irradiation, and thus can be used in known applications utilizing such a property, including, for example, photoactivity, bacteria prevention, hydrophilization, stain prevention, anti-fogging, gas decomposition, deodorization, water treatment, and energy conversion.

25 [0050]

Photoelectrodes for dye-sensitized solar cells are described below as an example of application of the semiconductor film according to the present invention.

[0051]

30 Generally, a dye-sensitized solar cell comprises a photoelectrode comprising a transparent substrate (e.g., a glass plate or high polymer film) provided on one side with an electrically conductive transparent layer (electrode) and semiconductor layer; a counter electrode facing the semiconductor  
35 layer on the electrode; and an electrolyte layer sandwiched



between the electrodes.

[0052]

The semiconductor layer is usually made of semiconductor particles, has pores, and supports a  
5 photosensitizing dye on the particle surfaces or in the pores.

[0053]

The electrically conductive transparent layer is formed on the surface of a glass plate, a high polymer film or like transparent substrate by vapor-depositing gold, silver, aluminum,  
10 indium, indium tin oxide (ITO), tin oxide or the like.

[0054]

The semiconductor film formed by the process of the present invention can be used as the semiconductor layer. The semiconductor layer is usually 1  $\mu\text{m}$  to 100  $\mu\text{m}$  thick, and  
15 preferably 2  $\mu\text{m}$  to 50  $\mu\text{m}$  thick.

[0055]

The photosensitizing dye can be selected from various known dyes that absorb light in the visible region and/or the infrared region of the spectrum.

20 [0056]

Examples of photosensitizing dyes include azo dyes, quinone dyes, quinoneimine dyes, quinacridone dyes, squarylium dyes, cyanine dyes, merocyanine dyes, triphenylmethane dyes, xanthene dyes, porphyrin dyes, phthalocyanine dyes, perylene dyes,  
25 indigo dyes, naphthalocyanine dyes, etc. Among these, metal complex dyes, such as phthalocyanine dyes and naphthalocyanine dyes, have a high quantum yield and high durability against light, and therefore are preferable as photoelectric conversion materials.

30 [0057]

Examples of metals to be combined with the photosensitizing dye include copper, nickel, iron, cobalt, vanadium, tin, silicon, titanium, germanium, cobalt, zinc, ruthenium, magnesium, aluminum, lead, manganese, indium,  
35 molybdenum, zirconium, antimony, tungsten, platinum, bismuth,

selenium, silver, cadmium, platinum, etc. Among these, copper, titanium, zinc, aluminum, iron, vanadium and silicon are preferable since metal complex dyes comprising these metals have a high quantum efficiency.

5 [0058]

The amount of the photosensitizing dye to be supported by the semiconductor particles is preferably  $10^{-8}$  mol/cm<sup>2</sup> to  $10^{-6}$  mol/cm<sup>2</sup>, and more preferably 0.1 to  $9.0 \times 10^{-7}$  mol/cm<sup>2</sup>. Less than  $10^{-8}$  mol/cm<sup>2</sup> of photosensitizing dye does not sufficiently improve  
10 the photoelectric conversion efficiency. More than  $10^{-6}$  mol/cm<sup>2</sup> of photosensitizing dye does not further improve the photoelectric conversion efficiency, increases the proportion of recombination of photoexcited electrons with holes, and thus is uneconomical.

15 [0059]

The electrolyte used in the electrolyte layer is not limited as long as it comprises a redox pair in a solvent. Preferably, the redox pair consists of an oxidant and reductant with the same electric charge. The redox pair is a pair of  
20 substances that reversibly exist in an oxidized or reduced form in an oxidation-reduction reaction system. Redox pairs are well known to persons of ordinary skill in the art. Examples of redox pairs include chlorine compound-chlorine, iodine compound-iodine, bromine compound-bromine, thallium ion (III)-thallium ion (I),  
25 mercury ion (II)-mercury ion (I), ruthenium ion (III)-ruthenium ion (II), copper ion (II)-copper ion (I), iron ion (III)-iron ion (II), vanadium ion (III)-vanadium ion (II), manganic acid ion-permanganic acid ion, ferricyanide-ferrocyanide, quinone-hydroquinone, fumaric acid-succinic acid, etc. Other redox pairs  
30 are also of course usable. Among the above redox pairs, iodine compound-iodine is preferable. Preferable iodine compounds include lithium iodide, potassium iodide, copper iodide, silver rubidium iodide and other metal iodides; tetraalkylammonium iodine, pyridinium iodine and other quaternary ammonium iodide  
35 salt compounds; dimethylpropylimidazolium iodide and other

diimidazolium iodide compounds; etc.

[0060]

The solvent to be used for dissolving the electrolyte is preferably a compound that dissolves the redox pair and has  
5 high ionic conductivity. An aqueous solvent and/or an organic solvent can be used, and an organic solvent is preferable to better stabilize the redox pair. Specific examples of organic solvents include dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, ethylene carbonate, propylene carbonate and  
10 other carbonate compounds; methyl acetate, methyl propionate,  $\gamma$ -butyrolactone and other ester compounds; diethyl ether, 1,2-dimethoxyethane, 1,3-dioxolane, tetrahydrofuran, 2-methyltetrahydrofuran and other ether compounds; 3-methyl-2-oxazolidine, 2-methylpyrrolidone and other heterocyclic  
15 compounds; acetonitrile, methoxyacetonitrile, propionitrile and other nitrile compounds; sulfolane, dimethylsulfoxide, dimethylformamide and other aprotic polar compounds; etc. Such solvents may be used singly or in combination. Especially preferable solvents include ethylene carbonate, propylene  
20 carbonate and other carbonate compounds; 3-methyl-2-oxazolidine, 2-methylpyrrolidone and other heterocyclic compounds; and acetonitrile, methoxyacetonitrile, propionitrile and other nitrile compounds.

[0061]

25 The electrolyte may be in the form of a liquid, solid or gel.

[0062]

An adhesive layer may be provided on the counter electrode layer, disposed opposite to the photoelectrode, of the  
30 dye-sensitized solar cell comprising a photoelectrode that comprises a transparent substrate (e.g., a glass plate or high polymer film) provided on one side with an electrically conductive transparent layer and semiconductor layer; an electrolyte layer; and a counter electrode layer facing the  
35 photoelectrode layer.

[0063]

An adhesive layer makes the solar cell attachable to various articles.

[0064]

5           The solar cell can be preferably attached to, for example, vehicles, buildings, constructions, roads, traffic signs, greenhouses and other structures that are likely to be exposed to sunlight.

[0065]

10           The solar cell may also be attached to a plastic plate, metal plate or like item by bringing the surface of the adhesive layer on the photoelectrode into contact with the item, followed by heating, compression, or compression with heating, to thereby bond the solar cell to the item. An item with a solar cell bonded  
15 thereto can be formed into a module by molding, cutting and/or other processes as required, followed where necessary by sealing of the cut portions.

[0066]

20           When the solar cell is intended to be cut, a solid or gel electrolyte is used therein.

[0067]

Examples of adhesives usable in the adhesive layer include known pressure-sensitive adhesives, heat-sensitive adhesives, curable adhesives, etc. Specific examples include  
25 thermosetting and thermoplastic adhesives comprising at least one resin selected from the group consisting of bisphenol-type epoxy resins, resol-type epoxy resins, acrylic resins, aminoplast resins, polyester resins, urethane resins, polysiloxane resins, (iso)butylene resins, vinyl acetate resins, vinyl chloride resins,  
30 vinyl chloride/vinyl acetate copolymers, synthetic rubbers, natural rubbers, etc.

[0068]

The adhesive layer is preferably 1  $\mu\text{m}$  to 1 mm thick, and more preferably 5  $\mu\text{m}$  to 500  $\mu\text{m}$  thick.

35           [0069]

[Effects of the Invention] The process of the present invention, in which a semiconductor particle dispersion liquid is applied by spray coating in such a manner that the atomized droplets of the dispersion liquid have a mean diameter of about

5 20  $\mu\text{m}$  or less, has the following remarkable advantages:

[0070]

1. When the semiconductor particle dispersion liquid is applied to a substrate, the semiconductor particles or small aggregates thereof form a semiconductor film, and thus the film  
10 is porous and has excellent adhesion to the substrate.

[0071]

2. In particular when ethanol is used as a solvent in the semiconductor particle dispersion liquid, the dispersion liquid is stable because of the high affinity of ethanol to the  
15 semiconductor particles. Therefore, the dispersion liquid, even when being subjected to a high shear stress at the time of spray coating, is unlikely to cohere at the nozzle tip and thereby clog the nozzle.

[0072]

20 3. Part of ethanol evaporates from the dispersion liquid during spray coating, the semiconductor particles being sprayed are stabilized.

[0073]

4. The high affinity of ethanol facilitates necking of  
25 the particles of the semiconductor particle dispersion liquid, and thus even when the dispersion liquid is applied to a flexible substrate such as a high polymer film, it does not peel off when the substrate flexes.

[0074]

30 5. In prior art techniques, a semiconductor particle dispersion liquid is applied to a glass plate or like substrate, and sintered at 200°C or higher to form a porous semiconductor film. In contrast, the process of the present invention is capable of forming a porous semiconductor film at low  
35 temperatures, and therefore can be applied to a substrate such as

a high polymer film.

[0075]

6. By microwave sintering of the semiconductor particle dispersion liquid applied to polyethylene terephthalate or like substrate, a film can be formed in which the semiconductor particles are uniformly sintered, even when the film has a large area.

[0076]

[Examples] The following Examples are given to illustrate the present invention in further detail, and are not intended to limit the scope of the invention. In these examples, parts and percentages are all by weight.

[0077]

#### Production Example of Titanium Oxide Particle Sol

Thirty parts of "P-25" (tradename of Japan Aerosil Co., Ltd., rutile-anatase-type titanium oxide ( $\text{TiO}_2$ ) crystals, mean primary particle size: 30 nm) and 120 parts of ethanol were dispersed using glass beads in a paint shaker for 6 hours, to thereby obtain a titanium oxide sol.

[0078]

#### Example 1

A polyethylene terephthalate (PET) sheet was spray-coated with the above titanium oxide sol under the coating conditions presented in Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is shown in Table 1.

The resulting coating was dried by heating at 150°C for 30 minutes, to thereby obtain a 8  $\mu\text{m}$  thick titanium oxide film.

[0079]

Table 2 shows the adhesion and scratch resistance of the obtained titanium oxide film.

[0080]

An electrically conductive PET (ITO) was under the conditions shown in Table 1, and baked in an electric furnace at 150°C for 30 minutes to obtain a 8  $\mu\text{m}$  thick porous titanium oxide

film. The porous film was immersed at room temperature overnight in an ethanol solution containing a sensitizing dye [Ru(2,2'-bipyridil-4,4'-dicarboxylate(TBA))<sub>2</sub>(NCS)] at a concentration of  $5 \times 10^{-4}$  M/L. The above-mentioned electrically conductive PET film  
5 sputtered with platinum was superimposed as the counter electrode on the sensitizing dye-adsorbing porous titanium oxide film. An electrolyte solution (40 mM iodine, 500 mM tetrapropylammonium iodine, 80 M ethylene carbonate and 20 M acetonitrile) was poured, to obtain a dye-sensitized solar cell. Table 2 shows the  
10 photoelectric conversion efficiency of the cell.

[0081]

The titanium oxide dispersion liquid was measured by the method of measuring the mean pore size (the same applies hereinafter), and found to be 14.9 nm, demonstrating that a  
15 preferable porous film was formed.

[0082]

Method of measuring the mean pore size: The titanium oxide dispersion liquid was applied to a PET film (10 x 10 cm) to a thickness of 5  $\mu$ m to 8  $\mu$ m, dried at 150°C for about 1 hour, and  
20 cut into strips (5 mm x 25 mm), and about sixty of the strips were inserted into a glass cell of "MICROMERITICS ASAP2010" (tradename of Shimadzu Corp., pore size distribution measuring apparatus utilizing nitrogen adsorption/desorption) to measure the mean pore size.

25 Example 2

Spray coating was performed under the coating conditions shown in Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is shown in Table 1.

30 [0083]

The resulting coating was dried by heating in an electric furnace at 150°C for 30 minutes.

[0084]

Table 2 shows the adhesion and scratch resistance of  
35 the obtained titanium oxide film.

[0085]

A dye-sensitized solar cell was obtained in the same manner as in Example 1 except for employing the coating conditions shown in Table 1. The photoelectric efficiency of the cell is shown in Table 2. The titanium oxide dispersion liquid was measured by the method of measuring the mean pore size (the same applies hereinafter), and found to be 14.5 nm, demonstrating that a preferable porous film was formed.

[0086]

10        Example 3

The procedure of Example 1 was followed except that microwave sintering as described below was performed at 180°C for 30 minutes in place of the drying by heating, to thereby obtain a 9  $\mu$ m thick titanium oxide film.

15        [0087]

The above-mentioned microwave sintering was performed using an electromagnetic wave thermal sintering apparatus (tradename "FMS-10-28", manufactured by Fujidenpa Kogyo Co., Ltd.) at a frequency of 28GHz, an output of 2 kW and an irradiation time of 2 minutes.

[0088]

The titanium oxide dispersion liquid was measured by the method of measuring the mean pore size (the same applies hereinafter) and found to be 15.5 nm, demonstrating that a preferable porous film was formed.

[0089]

Comparative Example 1

The titanium oxide particle dispersion liquid was applied with a knife coater and dried by heating in an electric furnace at 150°C for 30 minutes to thereby obtain a 8  $\mu$ m thick porous titanium oxide film.

[0090]

Table 2 shows the adhesion and scratch resistance of the obtained titanium oxide film. The titanium oxide dispersion liquid was measured by the method of measuring the mean pore size



(the same applies hereinafter) and found to be 9.5 nm, demonstrating that an inferior porous film was formed.

[0091]

#### Comparative Example 2

5           Spray coating was carried out under the conditions shown in Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is shown in Table 1.

[0092]

10           The resulting coating was dried in an electric furnace at 150°C for 30 minutes to thereby obtain a 10  $\mu$ m thick titanium oxide film.

[0093]

15           Table 2 shows the adhesion and scratch resistance of the obtained titanium oxide film. The mean pore size of the porous titanium oxide film was measured by the method of measuring the mean pore size, and found to be 10.5 nm, demonstrating that an inferior porous film was formed.

[0094]

20           Test methods

Photoelectric conversion efficiency (%): Measured using an artificial sunlight (xenon lamp) (JIS A.M.1.5, unit: 100 mW/cm<sup>2</sup>).

[0095]

25           Adhesion: A porous film that did not peel off even when the PET film with the porous film formed thereon was sharply bent or forcefully hit was evaluated as having good adhesion, while a porous film that peeled off when the PET film with the porous film was bent was evaluated as having poor adhesion.

30           [0096]

Film scratch resistance: Titanium oxide films were formed in the same manner as in the Examples and Comparative Examples except for using, as the substrate, a glass plate in place of the PET film, and used as test samples.

35           [0097]

Using a "Tribogear Type 18L" (tradename of Shinto Scientific Co., Ltd.), the load at which the glass plate was uncovered was found by applying a vertical load of 0 to 100 g to a scratch needle (made of sapphire, 1.2 mm in diameter) and moving the needle at a rate of 600 mm/min over a distance of 100 mm. The greater the load, the higher the scratch resistance. A load of 10 gf or more is particularly preferable.

[0098]

[Table 1]

10 Table 1

	Discharged amount (g/min)	Atomization air pressure (kgf/cm <sup>2</sup> )	Number of Stages (st)	Nozzle- substrate distance (mm)	Coating rate (m/min)	Cover- ing Pitch (mm)	Mean diam- eter (μm)	Film thick- ness (μm)
Ex.1	60	3.0	3	20	60	15	19.7	8
Ex.2	60	2.0	3	20	60	15	24.3	9
Ex.3	60	2.0	3	20	60	15	19.5	9
Comp. Ex.2	60	1.0	3	20	60	15	41.4	10

[0099]

[Table 2]

Table 2

	Conversion efficiency	Adhesion	Scratch resistance
	(%)		(gf)
Ex. 1	2.1	Good	14.1
Ex. 2	1.6	Good	12.6
Ex. 3	2.8	Good	12.6
Comp.Ex. 1	-	Poor	6.1
Comp.Ex. 2	-	Poor	7.3

[Document Name] Abstract

[Abstract]

[Objects] To provide a process for forming a semiconductor film, and a photoelectrode.

- 5 [Means for Achieving the Objects] A process for forming a semiconductor film, comprising the step of applying a semiconductor particle dispersion liquid to a surface of a high polymer film substrate by spray coating in such a manner that the atomized droplets of the dispersion liquid discharged from the
- 10 spray coater have a mean diameter of 20  $\mu\text{m}$  or less; and a semiconductor film obtained by the process and used for photoactivity, bacteria prevention, hydrophilization, stain prevention, anti-fogging, gas decomposition, deodorization, water treatment, or energy conversion; and a photoelectrode comprising
- 15 a laminate that comprises a transparent high polymer film layer, transparent electrode layer and a semiconductor film obtained by the above process.

[Selected Figure] None.